with either $|\mp\frac{9}{2}\rangle$ or $|\pm\frac{15}{2}\rangle\rangle$ lies 44 cm^{-1} above the ground state.[6]

An Orbach process is therefore expected[7] in the relaxation rate. The observed value of $1/T_1$ as a function of temperature should thus be fitted by a curve of one of the following forms:

$$1/T_1 = A'T + Be^{-\Delta/kT} \tag{1}$$

or

$$1/T_1 = DT^2 + Be^{-\Delta/kT}, \tag{2}$$

depending on whether a direct or phonon-limited (or bottleneck) process, respectively, dominates at low temperatures.[7]

The data are plotted as a function of temperature in Fig. 1 for a sample of concentration of 0.2%. The experimental points are fitted by the curve

$$1/T_1 = (2.5\pm0.2)T^2 + 1.6\times10^{11}e^{-(44\times1.44)/T}. \tag{3}$$

The value of Δ experimentally determined by curve fitting is 44 cm^{-1}, with an accuracy of 10%. It agrees well with the position of the first excited level determined optically by Erath.[6]

The data for higher concentrations, 10 and 100%, are plotted in Fig. 2 as a function of temperature. Note that the experimental value of D increases from 2.5/sec (deg K)^2 for 0.2% concentration to 22/sec (deg K)^2 for 100% concentration. However, it does not agree with the calculated value of D [50/sec (deg K)^2 for 0.2% concentration] using the expression of Scott and Jeffries.[7]

The relaxation time was also measured for different orientations of the c axis with respect to the steady magnetic field. At the lowest temperature of 1.1°K, the relaxation rate increased monotonically from 2.5 to 20 sec^{-1} as the angle between the c axis and the static magnetic field was increased from 0° to 90° for 0.2% concentration. No anomalous speedup was found at any angle, as is found with the Nd^{3+} LaES.[7]

Grateful thanks are due Dr. E. Y. Wong for showing the method of sample preparation.

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Optical Third-Harmonic Generation in Dye Solutions[*]

R. K. Chang[†] and Lee K. Galbraith
Dunham Laboratory, Yale University, New Haven, Connecticut

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The dependence of optical third-harmonic generation (THG) on the concentration of fuchsin and methylene blue dissolved in several solvents of different dispersions has been observed. The dye concentrations necessary to phase-match the liquid medium were found to vary in proportion to the dispersion of the pure solvent. At these phase-matched concentrations, the THG peak intensities for each dye were found to be equal. A simple model is suggested for the observed THG dependence on dye concentration and on dispersion.

I. INTRODUCTION

The observation of optical third-harmonic generation (THG) in solids, liquids, and gases has been previously reported.[1–3] The use of anomalous dispersion to achieve index matching at the fundamental and harmonic wavelengths has been proposed by several authors.[1,4–6] Experimental evidence of such compensation for solvent dispersion with anomalous dispersion of dissolved dyes has been recently reported by Bey, Giuliani, and Rabin[2] (BGR). In particular, a peak in the THG was observed when the dye concentration was at the value where index matching or phase matching between the Nd:glass laser wavelength and the THG wavelength was achieved.

Our experimental results confirm the findings of BGR and extend their work to other solvents of different index mismatch and to another dye, methylene blue. A simple model is suggested which accounts for the gross features of the observed THG dependence on dye concentration and on index dispersion of the pure solvents.

II. EXPERIMENTAL

To offset any possible effects of the multimode structure of laser emission and the recently reported picosecond pulses of gigawatt power which might be

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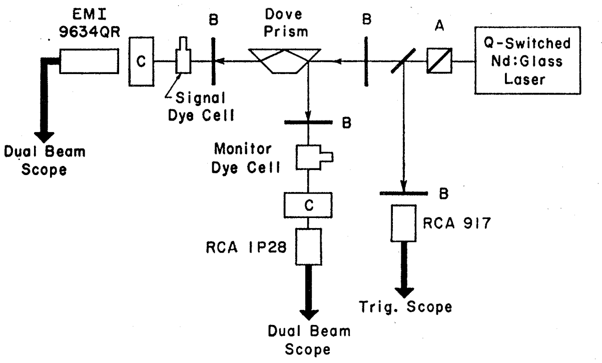

FIG. 1. Schematic diagram of the experimental arrangement for detecting THG and monitoring laser beam intensity by another THG optical dye cell. (A) Glan prism polarizer; (B) RG-10 and neutral density filters; (C) $CuSO_4$ cell and interference filter, 3530 Å. Sample dye cell is 0.05 cm and monitor dye cell is 1.00 cm in thickness.

superimposed on the main Q-switch laser pulse,[7] THG was normalized against the laser output as monitored by the amount of THG produced in a fixed nonlinear medium.[8] Specifically, the monitor was an optical cell (of 1.00 cm thickness) with fuchsin (color index No. 42500) dissolved in hexafluoroacetone sesquihydrate[2] (HS) at 60 g/liter. For each laser firing, the THG produced in this monitor cell was compared with that from the sample cell (of 0.05 cm thickness) containing dyes of specified concentrations in the chosen solvent mixtures.

A schematic diagram of the apparatus is shown in Fig. 1. The rotating prism Q-switched Nd:glass laser emission is first linearly polarized, then split into two paths by a Dove prism. The portion of the unfocused laser beam is incident on the sample dye cell. The THG from both cells was isolated from the 1.06-μ laser radiation by $CuSO_4$ solution filters plus 3530 Å interference filters. The THG outputs of the dye cells were detected by photomultipliers, and displayed on a dual beam oscilloscope. Fluctuation in the ratios of the two signals amounted to less than 10% for a given set of conditions.

III. RESULTS

Experimental data have been obtained from various dye concentrations of fuchsin and methylene blue (color index No. 52015) dissolved in three solvents of different index dispersion. The three solvents used—HS, two parts HS mixed with one part H_2O, and methanol—all have increasingly larger index mismatch between 1.06 and 0.353 μ. Figure 2 shows the sharp enhancement of the THG intensity as a function of fuchsin concentration in HS, F(HS), similar to the data presented by BGR. These authors have attributed the THG intensity peak to index matching of the liquid medium as a result of the anomalous dispersion of fuchsin. The critical concentration for the intensity peak is approximately 45 g/liter, as shown in Fig. 2. Upon addition of H_2O to pure HS in the proportion of ($\frac{2}{3}$ HS+$\frac{1}{3}$ H_2O), the index mismatch for this binary mixture becomes larger than that of HS. It is obvious that the dye concentration necessary to bring about index matching in this binary mixture should be larger. The data shown in Fig. 2 for F($\frac{2}{3}$ HS+$\frac{1}{3}$ H_2O) has a critical concentration for a THG intensity peak at about 65 g/ liter. Similar displacement of the THG peak versus concentration is observed when methylene blue is dissolved in HS and ($\frac{2}{3}$ HS+$\frac{1}{3}$ H_2O) as shown in Fig. 3. The critical concentration necessary for index matching shifted from 55 to 80 g/liter, which is the same ratio as that for F(HS) and F($\frac{2}{3}$ HS+$\frac{1}{3}$ H_2O). Figure 3 further shows that when methylene blue is dissolved in methanol, which has the largest index mismatch of the three solvents, the critical concentration needed for the THG peak was found at 140 g/liter. Unfortunately, the solubility of fuchsin in methanol is below 72.5 g/liter. In H_2O, the solubility of both these dyes is less than 40 g/liter.[9]

For a given dye, Figs. 2 and 3 show that the measured THG intensities at the critical concentrations required

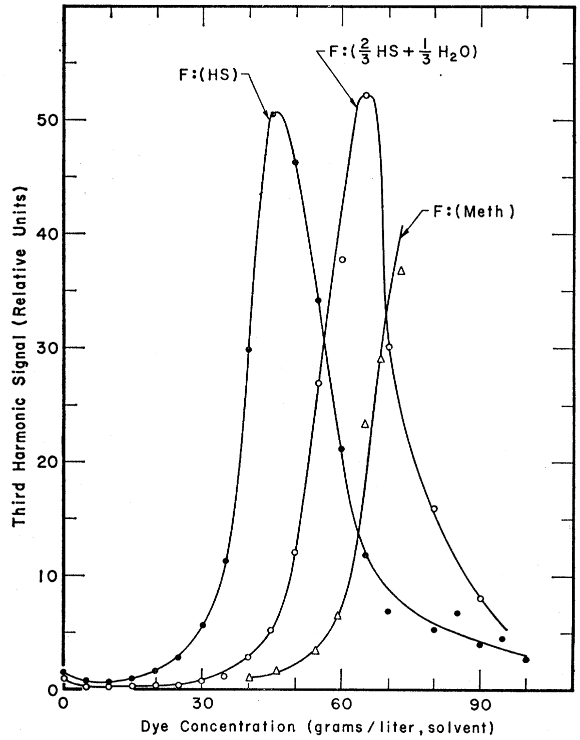

FIG. 2. Relative THG intensity as a function of fuchsin concentrations in various solvents: HS, ($\frac{2}{3}$HS+$\frac{1}{3}$$H_2O$), and methanol.

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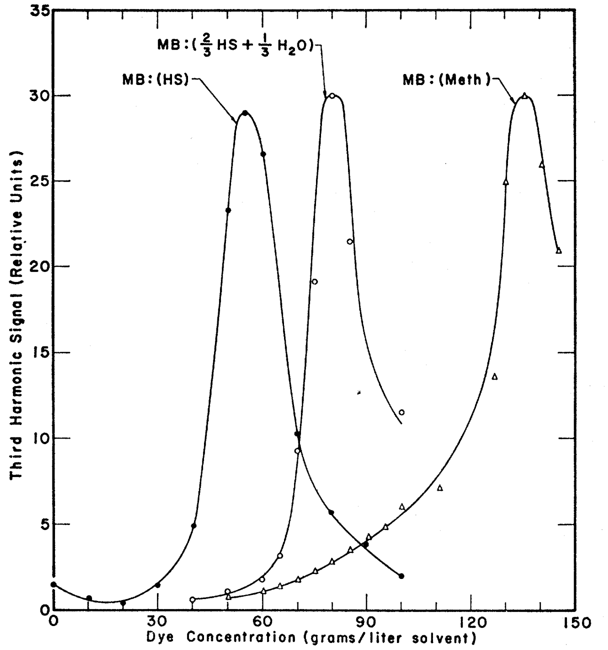

FIG. 3. Relative THG intensity as a function of methylene blue concentration in various solvents: HS, ($\frac{2}{3}$HS+$\frac{1}{3}$H$_2$O), and methanol.

for index matching of the three solvents are all equal within our experimental errors of 10–15%. At these critical dye concentrations, the THG intensity from fuchsin dye is 1.7 times larger than that from methylene blue.

A simple model will be presented in Sec. IV which agrees qualitatively with the observed shift of the critical dye concentration with index mismatch of solvents, as well as the independence of the THG intensities from the critical dye concentrations that yield intensity peaks due to index matching.

IV. DISCUSSION

Both fuchsin and methylene blue have strong linear absorptions between the fundamental and the third harmonic wavelengths. The absorption maximum occurs at 570 mμ for fuchsin, and at 650 mμ for methylene blue. The absorption at the third harmonic wavelength, although much weaker than the absorption maximum in each case, is large compared to that at the fundamental wavelength. Consequently, near the phase-matched condition, the THG intensity will not exhibit the oscillatory behavior characteristic of large-index matched paths in fully transparent media as a function of effective optical path length[4] (readily varied by tilting the dye cell).

If the absorption at 3ω is significant, while negligible at ω, the following expression is readily derived[2]:

$$I^{3\omega} \propto \frac{|c\chi_0^{\mathrm{NL}}|^2}{(\Delta K)^2+\frac{1}{4}(c\alpha_0^{3\omega})^2}. \qquad (1)$$

Let us assume that the phase mismatch of the liquid medium is linear in the dye concentration c, so that, using Beer's law,

$$\Delta K = 6\pi(n^{3\omega}-n^{\omega})/\lambda = (6\pi/\lambda)\Delta n_{\mathrm{ps}}(1-\beta c/\Delta n_{\mathrm{ps}}). \qquad (2)$$

The quantity χ_0^{NL} is the nonlinear susceptibility of the liquid medium *per unit concentration* of dye. The phase mismatch of the liquid medium at dye concentration c is ΔK. The index mismatch Δn_{ps} is that of the pure solvent. The phenomenological constant β represents the effectiveness of the dye in bringing about index matching by anomalous dispersion. The absorption constant of the liquid medium *per unit dye concentration* is $\alpha_0^{3\omega}$, while $n^{2\omega}$ and n^{ω} are the index of refraction at 3ω and ω of the liquid medium. The fundamental wavelength λ is 1.06 μ.

A comparison is made in Fig. 4 between the measured THG dependence and the expression of Eq. (1). The dashed curves are computed from Eq. (1), for the same values of χ_0^{NL},β, and $\alpha_0^{3\omega}$ for all the three solvents. The solid curves are the same experimental curves shown perviously in Fig. 2. The index mismatch values of 0.014, 0.020, and 0.025 are used for the following pure solvents: HS, ($\frac{2}{3}$ HS+$\frac{1}{3}$ H$_2$O), and methanol. The absorption constant at 3ω is determined by a spectro-

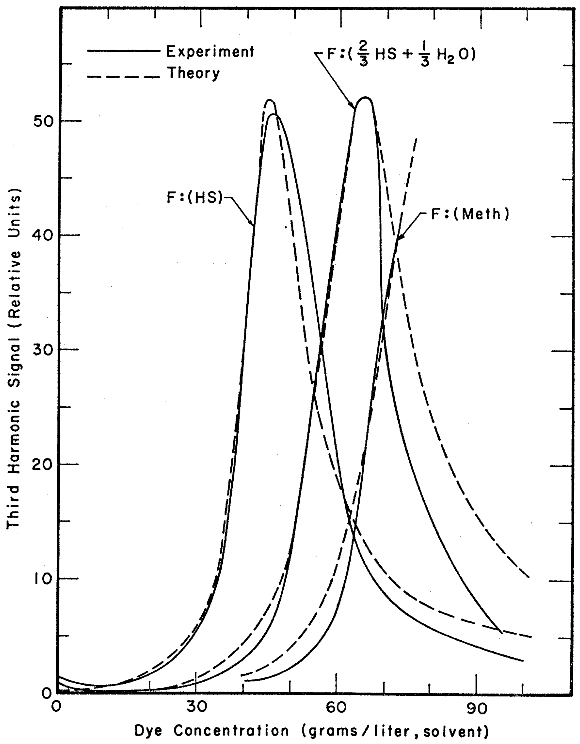

FIG. 4. Relative THG intensity as a function of fuchsin concentrations in various solvents. The solid experimental curves are the same as those shown in Fig. 2. The dashed curves are computed from Eq. (1) using the same χ_0^{NL}, β, and $\alpha_0^{3\omega}$ for all solvents. The index mismatch of 0.014, 0.020, and 0.025 is used for HS, $\frac{2}{3}$HS+$\frac{1}{3}$H$_2$O, and methanol, respectively.

photometer and is found to be $\alpha_0^{3\omega}=20$ cm^{-1} g^{-1} liter. The phenonmenological constant β is determined from the experimental data of fuchsin dissolved in HS, and is found to be $\beta=3.1\times10^{-4}$ g^{-1} liter. This same value of β is used in the computed curves for fuchsin dissolved in the other two solvents. Since only the relative THG intensity is measured, the value of χ_0^{NL} is chosen to normalize the computed curves for F(HS) to 52 arbitrary units at the THG peak. Again, this same value was used for the other two solvents. The agreement is good for the simple level of approximation we have taken, which thus accounts for the qualitative features. Equations (1) and (2) lead to the following features:

(1) We expect that at the critical concentration (i.e., for a peak in THG), $c_p=\Delta n_{ps}/\beta$, should vary linearly with the index mismatch of the pure solvents. Our experimental results on c_p for the two dyes dissolved in HS and ($\frac{2}{3}$ HS+$\frac{1}{3}$ H_2O) agree with this approximation, but our measured c_p value for methylene blue in methanol occurred at a larger concentration (140 g/liter) than expected from the index mismatch of mathanol (100 g/liter). Actually, one would expect β to be slightly solvent and concentration-dependent. In fact, THG versus dye concentration might be an independent measure of the strength of the dye in bringing about index matching in various liquids.

(2) At the critical dye concentrations, where $\Delta K=0$, the THG intensity is proportional to $|\chi_0^{\mathrm{NL}}/\alpha_0^{3\omega}|^2$. This quantity should be concentration independent, as both χ_0^{NL} and $\alpha_0^{3\omega}$ are defined as parameters normalized by dye concentration, and are assumed to be constant for a given dye, with different solvents and dye concentrations over a wide range. Within our experimental error, the THG peak intensity for each dye shown in Figs. 2 and 3 is the same. (At very large concentrations, approaching the solubility saturation level, one might expect χ_0^{NL} and $\alpha_0^{3\omega}$ to exhibit some dependence on the dye concentration, thus deviating from Beer's law.)

(3) When the dye concentration exceeds twice the critical concentration, the THG intensity is expected to approach an asymptotic value which is again concentration-independent. Our experimental results on F(HS) tend to confirm this trend.

So far in the discussion, the nonlinear contributions from the optical cell windows and pure solvents have been neglected. For the two dyes we have examined, this is a fair approximation at dye concentrations above 30 g/liter. However, THG has been detected from a cell containing only pure solvents, as shown in Figs. 2 and 3. Upon addition of small amounts of dye, the THG always decreased from that measured when the cell contained only pure solvents. One can account for this decrease of THG if the nonlinear susceptibility of the dye has an antiphase[10] with respect to that of the cell windows and pure solvent.

By way of comparison with past THG measurements in solids, the energy conversion, in phase-matchable calcite, from fundamental to THG, was stated[1] to be 3 ppm, with a laser intensity of approximately 10^7 W/cm^2 focused by a 25-cm focal-length lens inside a 4-mm-thick crystal. Our estimate for the detected THG intensity from index matched fuchsin is approximately 10^{-5} W/cm^2, when an unfocused laser beam of 10^7 W/cm^2 is incident on the dye cell. Had we focused our laser beam to increase intensity by 100:1, the energy conversion then could be comparable to that of calcite, which requires angular orientation of the crystals to achieve phase matching.

In order to maximize the THG, liquid medium with larger nonlinear susceptibility, χ_0^{NL}, and lower absorption at 3ω, should be sought. To this end, THG from several highly water soluble xanthene dyes (eosin *B*, eosin *Y*, rose bengal, phloxine, and erythrosin) were examined. All these liquid media failed to give much THG, in spite of the fact that their linear absorption is large, near 2ω, and small at ω and 3ω.

V. CONCLUSION

Our experimental results have confirmed and extended the initial work of BGR. The concentration dependence of the THG from fuchsin and methylene blue dissolved in three solvents of different index mismatch have been examined. The gross feature of our experiments are qualitatively accounted for by a simple expression for the THG. Further experiments are planned to study the effects of resonance near and at 2ω on the enhancement of the THG nonlinear susceptibility[11] both in liquids and solids.

ACKNOWLEDGMENT

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